1 260 933

PATENT SPECIFICATION

(11) 1 260 933

DRAWINGS ATTACHED

(21) Application No. 17894/69 (22) Filed 8 April 1969
(31) Convention Application No. P 17 71 143.2
(32) Filed 10 April 1968 in
(33) Germany (DT)
(45) Complete Specification published 19 Jan. 1972
(51) International Classification C 03 c 3/22, 3/12 // 27/02; C 04 b 37/04
(52) Index at acceptance
C1M 11B3 11C1 11C4 11C5 11C6 11F1 11F34 11H 11K1 19A1 19D8D 19E1 19E3D 19E4C D27 S5

(54) METHOD OF MANUFACTURING A GLASS CERAMIC MATERIAL

(71) We, PHILIPS ELECTRONIC AND ASSOCIATED INDUSTRIES LIMITED, of Abacus House, 33 Gutter Lane, London, E.C.2, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a method of manufacturing a glass ceramic material which is resistant to attack by sodium vapour and also relates to discharge lamps either in which the connection between an envelope made of a densely sintered polycrystalline material, for example, aluminium oxide, and the electrode metal consists of the glass ceramic material manufactured by said method, or in which the envelope itself consists wholly or partly of said glass ceramic material.

Densely sintered polycrystalline aluminium oxide, (U.S. Patent Specification No. 3,026,210) comprises at least 99.5% of Al_2O_3. It is translucent, gas-tight and has an excellent resistance to attack by sodium vapour up to very high temperatures. This material is therefore used as an envelope for high pressure sodium vapour discharge lamps.

The sealing of said lamps and the sealing-in of the electrodes was not so simple up till now. It was proposed *inter alia* (U.S. Patent Specification No. 3,281,309) to use for this purpose melted eutectic mixtures on the basis of alkaline earth metal oxide and Al_2O_3, which upon solidification produce a vitreous crystalline product. The crystalline phases in most of the compositions of this type are formed spontaneously and rapidly, and so uncontrolled. As a result of this the mechanical rigidity and the gas-tightness of the resulting connection is strongly reduced. Actually, said material can only be useful as a cement and is unfit for the manufacture of rather large bodies.

In manufacturing sodium vapour discharge lamps, it was hitherto necessary to use terminating or inserting members of densely sintered polycrystalline aluminium oxide. The result of this is that due to the matching of the coefficients of expansion, the metal must consist of niobium, which has the drawback that sealing together has to be carried out in a rare gas.

According to the method of the invention, a glass ceramic material is manufactured which is resistant to the action of sodium vapour and in which the crystalline phase is very fine-granular. This glass ceramic material is therefore not only suitable as a readily adhering gas-tight sealing material, but is also suitable for manufacturing bodies.

The present invention provides a method of manufacturing a glass ceramic material which is resistant to attack by sodium vapour, wherein a glass having a composition expressed in % by weight within the following ranges:—

CaO	24—50
Al_2O_3	35—57.5
MgO	0—12
BaO	0—16
Y_2O_3	0—10
B_2O_3	0—9
ZrO_2	0—17.5
Li_2O	0—3
wherein ($B_2O_3+ZrO_2+Li_2O$)	3—20,

is first heated for 30 to 120 minutes at a temperature between 700 and 900°C, then from 0 to 120 minutes between 900 and 1000°C and finally for 60 to 360 minutes between 1000 and 1200°C.

The resulting glass ceramic material, which is finely crystalline, has a sodium vapour resistance, as compared with glass of the same composition, which is satisfactory up to temperatures which are approximately 200°C higher than for the glass, that is to say up to approximately 900°C. It is not suitable for an envelope of a high pressure sodium vapour discharge lamp. On the other hand, it may

[Price 25p]

be used as an envelope when medium pressures are used. A number of glass ceramic materials within the above range of compositions have a translucency which is comparable to that of densely sintered aluminium oxide. They are suitable for being processed, for example, to tubular bodies by means of the extrusion method, which is described in our co-pending Application No. 48,318/68 (Serial No. 1,240,273).

According to a preferred embodiment of the method according to the present invention, a glass having a composition expressed in % by weight within the following ranges:—

CaO	30—50
Al_2O_3	35—55
MgO	2—7
BaO	4—16
Y_2O_3	0—10
B_2O_3	3—9
ZrO_2	0—10,

is first heated for 30 to 120 minutes at a temperature between 700 and 900°C, then for 30 to 120 minutes between 900 and 1000°C, and finally for 60 to 240 minutes between 1000 and 1200°C.

The treatment in three stages, that is to say including a treatment at a temperature between 900 and 1000°C between the formation of nuclei and the nuclei growth, reduces the danger of the formation of cracks in the material considerably.

In manufacturing high pressure sodium vapour lamps, having an envelope of densely sintered polycrystalline aluminium oxide, the glass ceramic material which is manufactured according to the invention presents the possibility of a much simpler sealing than the one used so far.

Figure 1 shows a known sealing. In this Figure, reference numeral 1 denotes the tubular envelope of densely sintered aluminium oxide, in which an annular member 3 of the same material is provided in a clamping manner at either end. A ring 4 likewise consists of the same material. Niobium is used as an electrode lead-in member 2, while two rings 5 consist of a compressed glass powder mixed with a binder. The glass has, for example, the composition (in % by weight): CaO 38.8; Al_2O_3 45.6; MgO 5.2; BaO 8.7 and B_2O_3 1.7, according to our United Kingdom Patent Serial No. 1,172,794. Upon heating, the binder burns away and forms a vacuum-tight connection between the envelope and the electrode lead-in member.

Figure 2 shows how the sealing with the material according to the present invention employs a much simpler construction than that shown in Figure 1. According to this method the plug of glass 7 which consists of one assembly is converted, after sealing-in, by a suitable thermal treatment into the glass ceramic material according to the invention. In this method of sealing the electrode lead-in member 6 may consist, for example, of molybdenum, which is much cheaper.

In carrying the invention into effect it has been found that in the first phase of the thermal treatment finely divided nuclei, for example, in the form of 3 $CaO.B_2O_3$ segregate in the glass. During the further thermal treatment the compound $CaO.Al_2O_3$ which is excellently resistant to the action by sodium vapour crystallizes on said nuclei. The resistance of a suitable glass ceramic material to attack by sodium vapour depends on the choice of the composition and of the temperature programme since in addition to $CaO.Al_2O_3$ the phase 12 CaO. $7Al_2O_3$ which is very poorly resistant to the action by sodium vapour may also be separated.

The material obtained according to the invention need not only be used as a sealing material for high pressure sodium lamps or for medium pressure sodium lamps, but can also be used for other high load lamps.

In order that the invention may readily be carried into effect, it will now be described in greater detail with reference to a few examples. The compositions summarized in the table in % by weight are melted from a mixture which contains calcium carbonate, aluminium oxide, and, if required, boric acid, lithium carbonate, magnesium carbonate, barium carbonate, zirconium oxide and yttrium oxide. Rods drawn from the melt are first heated at a temperature between 750 and 850°C for 2 hours. The temperature is then raised at a rate of 4 to 5°C per minute to 950°C and kept at this value for one hour. The temperature is then increased once again at a rate of 4 to 5°C per minute to 1100°C, kept at the last-mentioned temperature for 2 to 4 hours, and finally cooled in air to room temperature.

Nr.	Composition % by weight											
	1	2	3	4	5	6	7	8	9	10	11	12
CaO	37,2	38,0	36,3	34,5	36,7	36,8	47,9	46,2	34,4	34,5	29,3	41,8
Al_2O_3	43,4	44,4	42,3	40,4	40,4	43,0	43,6	46,9	40,2	50,3	46,7	52,0
MgO	4,9	2,8	2,6	2,5	2,7	5,9	—	—	4,5	—	7,9	—
BaO	8,3	8,5	8,2	7,9	8,3	8,2	—	—	15,3	—	—	—
B_2O_3	6,2	6,3	6,0	5,7	6,1	6,1	8,5	6,9	5,6	—	—	—
ZrO_2	—	—	4,6	9,0	—	—	—	—	—	15,2	16,1	4,2
Y_2O_3	—	—	—	—	5,8	—	—	—	—	—	—	—
Li_2O	—	—	—	—	—	—	—	—	—	—	—	2,0

The phases 3 $CaO.B_2O_3$ and $CaO.Al_2O_3$ can be detected in an X-ray diffraction pattern in the final product. The phase 12 CaO.7 Al_2O_3 is present in traces.

The sodium resistance is very good for all samples after a treatment at 850°C for 48 hours. In the samples 1, 2, and 6, such a load at 950°C causes hardly any attack.

WHAT WE CLAIM IS:—

1. A method of manufacturing a glass ceramic material which is resistant to attack by sodium vapour, wherein a glass having a composition expressed in % by weight within the following ranges:—

CaO	24—50
Al_2O_3	35—57.5
MgO	0—12
BaO	0—16
Y_2O_3	0—10
B_2O_3	0—9
ZrO_2	0—17.5
Li_2O	0—3
wherein ($B_2O_3+ZrO_2+Li_2O$)	3—20,

is first heated for 30 to 120 minutes at a temperature between 700 and 900°C. then for 0 to 120 minutes between 900 and 1000°C, and finally for 60 to 360 minutes between 1000 and 1200°C.

2. A method as claimed in Claim 1, wherein a glass having a composition expressed in % by weight within the following ranges:—

CaO	30—50
Al_2O_3	35—55
MgO	2—7
BaO	4—16
Y_2O_3	0—10
B_2O_3	3—9
ZrO_2	0—10,

is first heated for 30 to 120 minutes at a temperature between 700 and 900°C, then for 30 to 120 minutes between 900 and 1000°C and finally for 60 to 240 minutes between 1000 and 1200°C.

3. A method of manufacturing a glass ceramic material which is resistant to attack by sodium vapour, substantially as herein described with reference to the specific examples.

4. The use of the glass ceramic material manufactured by the method as claimed in any of Claims 1 to 3 as a sealing material for high pressure sodium vapour discharge lamps, employing an envelope formed from densely sintered polycrystalline aluminium oxide having a purity of at least 99.5%.

5. The use of the glass ceramic material manufactured by the method as claimed in any of Claims 1 to 3 as an envelope for discharge lamps.

6. A glass ceramic material manufactured by the method as claimed in any of Claims 1 to 3.

C. A. CLARK,
Chartered Patent Agent,
Century House, Shaftesbury Avenue,
London, W.C.2.
Agent for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1972.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

1260933 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

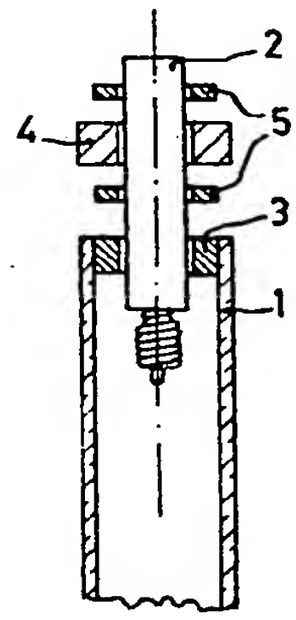

fig.1

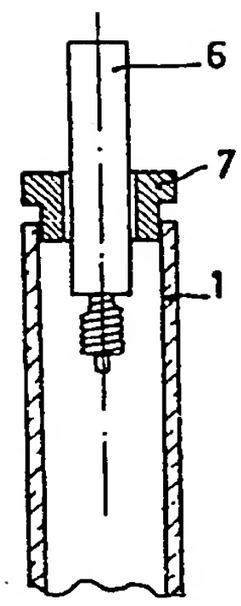

fig.2